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The digallane molecule, Ga₂H₆: experimental update giving an improved structure and estimate of the enthalpy change for the reaction Ga₂H₆(g) → 2GaH₃(g)^{†‡}

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Improved methods of analysis and new quantum chemical calculations have been applied to the results of earlier gas-phase electron diffraction (GED) studies of digallane to give what is judged to be the most realistic structure available to date. The principal distances ($r_{a3,1}$ in pm) and interbond angles ($\angle_{a3,1}$ in deg) are as follows (t = terminal, b = bridging): $r(\text{Ga} \cdots \text{Ga})$ 254.9(2), $r(\text{Ga}-\text{H}_t)$ 155.0(6), $r(\text{Ga}-\text{H}_b)$ 172.3(6), $\angle\text{Ga}-\text{H}_b-\text{Ga}$ 95.4(5), and $\angle\text{H}_t-\text{Ga}-\text{H}_t$ 128.6(9). Scrutiny of the IR spectra of solid Ar matrices doped with the vapour above solid samples of gallane at temperatures in the range 190–220 K reveals the presence of not only Ga₂H₆ as the major component, but also a significant fraction of the monomer GaH₃. Analysis of the relative proportions of the two molecules evaporating from the solid at different temperatures has led to a first experimental estimate of $59 \pm 16 \text{ kJ mol}^{-1}$ for the enthalpy change associated with the reaction Ga₂H₆(g) → 2GaH₃(g). Together with a value of 52 kJ mol^{-1} delivered by fresh calculations at the MP2 level, this implies that the stability of the dimer with respect to dissociation has been overrated by earlier theoretical treatments.

Introduction

The story of gallane, GaH₃, the binary hydride of gallium most stable at normal temperatures, begins with a claim made by Wiberg *et al.* nearly 70 years ago.¹ Not until 1989,² however, did the literature afford the first reported synthesis (from monochlorogallane, [H₂GaCl]_n, and lithium tetrahydrogallate, LiGaH₄) of a more or less pure sample of this labile compound, which decomposes to the elements at ambient temperatures. A fuller account of not only the synthesis but also some of the physical and chemical properties, appearing in 1991,³ included the results of gas-phase electron diffraction (GED) experiments carried out on the vapour at *ca.* 255 K. The GED pattern could be interpreted on the basis of a model consisting of a diborane-like molecule, H₂Ga(μ-H)₂GaH₂, for which an r_a structure was determined. The IR spectrum of the gaseous compound³ and the IR and Raman spectra of solid noble gas or nitrogen matrices doped with the vapour^{3,4} are uniformly consistent with such a structure, as is the valence-shell

photoelectron spectrum of the vapour.⁵ Review articles^{6–9} have described the methodology of the research as well as setting gallane in the wider context of main group metal hydrides. More recent studies have shown that Ga₂H₆ is also formed, along with GaH₃, among the products when a solid matrix formed by co-depositing laser-ablated Ga atoms with hydrogen at 3.5 K is exposed to mercury arc radiation.¹⁰ Similar experiments with other group 13 metal atoms identified the formation of the elusive molecules Al₂H₆¹¹ and In₂H₆,¹² but not of Tl₂H₆,¹³ they have also affirmed the predicted¹⁴ instability of indane, even at temperatures as low as 180–190 K.¹²

At the time when the GED study of digallane was performed, there was little guidance available from high-level quantum chemical calculations on the molecule. The first *ab initio* studies carried out at the SCF level using basis sets of slightly less than triple zeta plus polarisation (TZP) quality were reported in 1989.¹⁵ Others, at the Hartree–Fock,^{16,17} MP2,^{16,17} MP4,¹⁶ and DFT^{10,18} levels, followed. The highest level calculations carried out so far appear to be those of Shen and Schaefer¹⁹ who employed the single and double excitation coupled cluster (CCSD) method with double-zeta plus polarisation (DZP) basis sets to predict a diborane-like structure for the Ga₂H₆ molecule with the following dimensions (r_e in pm and \angle_e in deg, t = terminal, and b = bridging): Ga \cdots Ga 260.8, Ga–H_t 155.2, Ga–H_b 175.3, and H_t–Ga–H_t 129.9.

Gallane condenses at low temperatures as a white solid that melts at *ca.* 223 K to form a colourless, viscous liquid which in turn decomposes to the elements at temperatures above 243 K.^{2,3,6} At a pressure of 10 mmHg the vapour has a half-life of about 2 min at ambient temperatures, although its decomposition is markedly subject to autocatalysis. This lability has hampered severely the experimental characterisation of the compound. Despite attempts

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[†]A paper dedicated to Professor David Rankin in friendship and warm appreciation of the outstanding contributions he has made in the field of structural chemistry

[‡]Electronic supplementary information (ESI) available: Table S1—experimental details from the reanalysis of the GED data; Table S2—full list of interatomic distances, amplitudes of vibration and distance corrections; Table S3—least-squares correlation matrix for the refinement of Ga₂H₆; Table S4—Cartesian coordinates from the final $r_{a3,1}$ GED refinement; Table S5—Cartesian coordinates calculated at the MP2(full)/aug-cc-pVTZ level; Figure S1—molecular-scattering intensity curves for the GED refinement. See DOI: 10.1039/c000694g

to grow single crystals at low temperature and to carry out X-ray and neutron diffraction studies on powder samples,²⁰ the structure of the solid has so far eluded characterisation. Its properties (and particularly its IR and Raman spectra)^{3,6,20} imply an oligomeric or, more likely, a polymeric structure, but one different from that of solid alane, α -AlH₃,²¹ in that it features not only Ga–H–Ga bridges, but also terminal Ga–H units. A possible model is suggested by the mixed hydride [GaBH₆]_n, the crystal structure of which at 110 K reveals helical chains made up of alternating pseudo-tetrahedral GaH₄ and BH₄ fragments.²² The IR spectrum of the vapour of gallane reveals under high resolution rotational structure, preliminary studies of which have afforded unmistakable evidence of a Ga₂H₆ molecule with a diborane-like structure and given some guidance as to its dimensions.³ A more detailed and extensive study may yet yield the most definitive structural details. Up to the present time, however, the earlier GED measurements³ have provided the sole experimental basis of structure determination for the Ga₂H₆ molecule. The lability and reducing action of the vapour combined to give GED patterns that were inevitably marred by an unusually high noise level. Modelling of the patterns was then performed with a harmonic force field that made no concessions to the true nature of deformation modes occurring at low wavenumber, and without any correction of the interatomic distances for the effects of “shrinkage”.²³ The resulting r_a structure³ must accordingly be judged a relatively basic one.

Here we report the results of new quantum-chemical calculations on the Ga₂H₆ molecule. These have yielded *inter alia* anharmonic force constants, which have then been introduced into the program SHRINK²⁴ to estimate amplitudes of vibration and associated distance corrections for each atom pair. All the independent geometric parameters were then refined using a least-squares method, with restraints applied through the SARACEN method²⁵ to parameters that could not otherwise be refined, to arrive at a structure for the molecule of the type $r_{a3,1}$.²⁶ This we judge to be the most reliable given the experimental data currently available. In addition, scrutiny of the IR spectra of Ar matrices doped with the vapour over solid samples of gallane at temperatures in the range 190–220 K, while confirming the presence of Ga₂H₆ as the major constituent, reveal also a small fraction of the monomer GaH₃ recognisable by the spectrum previously reported.^{10,27} On this evidence, as the temperature of the solid changes, the relative proportions of monomer and dimer vary in such a way as to furnish, albeit roughly, a first experimental estimate of the dissociation enthalpy of the Ga₂H₆ molecule.

Experimental and computational details

Preparation, manipulation and spectroscopic studies

Rigorously pre-conditioned all-glass apparatus was used to synthesise isotopically natural or perdeuterated samples of gallane by the reaction of monochlorogallane, [H₂GaCl]_n, with freshly prepared lithium tetrahydrogallate, LiGaH₄ or LiGaD₄, at *ca.* 250 K, and for the subsequent purification and manipulation of the compound. Relevant details of the procedures have been described elsewhere.^{3,6} In order to measure the IR spectrum of a solid Ar matrix incorporating the vapour of the compound, an all-glass inlet system, consisting of a jacketed, single-sleeved tube, connected an ampoule containing a sample of the solid gallane

to the matrix apparatus described previously.^{3,4,28} The jacket and sleeve combination facilitated uniform cooling of the inner nozzle through the turbulence created in the flow of the coolant gas (N₂), thereby ensuring that the inlet system could be held at a temperature ≤ 243 K so as to avoid any decomposition of the gallane vapour.⁴ The Ar matrix gas was used as supplied (by BOC, research grade). Each experiment with the gallane sample ampoule at a different temperature was carried out in an identical fashion with the matrix gas being deposited at a rate of 2 mmol h^{−1} over a period of 1–2 h. IR spectra of the matrix samples were recorded at a resolution of 0.5 cm^{−1} and with an accuracy of ± 0.1 cm^{−1} using a Nicolet Magna-IR 560 FTIR instrument equipped with a liquid-N₂-cooled MCTB detector covering the spectral range 4000–400 cm^{−1}.

Computational methods

Quantum chemical calculations were performed using the resources of the NSCCS²⁹ running the Gaussian 09 suite of programs.³⁰ With D_{2h} point-group symmetry assumed, geometry optimisations were run for Ga₂H₆ using the MP2(full) method,³¹ with 6-31G*,³² aug-cc-pVDZ and aug-cc-pVTZ³³ basis sets. In order to calculate the enthalpy change associated with Ga₂H₆(g) \rightarrow 2GaH₃(g), calculations were also performed for GaH₃ (assuming D_{3h} symmetry) at the MP2(full)/aug-cc-pVTZ level. The basis-set superposition error (BSSE) was also calculated at this level of theory using the counterpoise method.³⁴ Harmonic and anharmonic vibrational frequencies calculated for Ga₂H₆ and Ga₂D₆ were in satisfactory agreement with experimental values, where comparisons could be made;^{3,4} the anharmonic force constants³⁵ calculated for Ga₂H₆ [MP2(full)/aug-cc-pVTZ] were introduced into the SHRINK program²⁴ to obtain starting values for amplitudes of vibration and distance corrections for use in the GED refinement.

Gas-phase electron diffraction

How the GED patterns of gallane were measured has been reported earlier.³ Again it was necessary to construct a special all-glass inlet assembly that could be cooled so as to avert possible decomposition of the gallane vapour *en route* to the chamber of the Edinburgh diffraction apparatus.³⁶ The temperature of the vapour used in the experiment was therefore as close to 255 K as was possible. The GED data used in this study were digitised from the original Kodak Electron Image plates on which they were recorded with the aid of an Epson Expression 1680 Pro flatbed scanner as part of a method that is now used routinely in Edinburgh, as described elsewhere.³⁷ Data-reduction and least-squares refinement processes were carried out using the ed@ed v3.0 program³⁸ employing the scattering factors of Ross *et al.*³⁹ The weighting points for the off-diagonal weight matrix, correlation parameters, and scale factors are given in Table S1.†

Results and discussion

The vibrational spectra of solid noble gas matrices doped with gallane vapour have already played an important part in establishing the identity and some of the vibrational properties of the Ga₂H₆ molecule.^{3,4,6} More recent studies of solid Ar matrices incorporating the vapour over *solid* samples of gallane held at

temperatures in the range 190–220 K have now revealed the previously unsuspected presence of the monomer GaH₃ as a minor but persistent component of the vapour, a finding of potential significance not only to the interpretation of the GED pattern of the vapour, but also to the thermodynamic stability of the dimer with respect to dissociation.

Matrix-isolation experiments

Fig. 1 illustrates the IR spectrum of an Ar matrix at *ca.* 20 K formed by co-condensing the matrix gas with the vapour over a sample of solid gallane held at 193 K. The main features of the spectrum agree well with those reported previously and associated with the Ga₂H₆ molecule.^{3,4} The most intense absorption is that at 676 cm⁻¹ [attributed to the δ(GaH₂) mode, ν₁₈ (*b_{3u}*) of Ga₂H₆] with other prominent absorptions occurring at 2015, 1996, 1983, 1965, 1280, 1221, 1205, 772, 761, 669/666/665, and 659/655/653/648 cm⁻¹. With due allowance for the effects of matrix splitting, all of these bands can be identified with IR-active vibrational fundamentals of the H₂Ga(μ-H)₂GaH₂ molecule on the assumption that it has a *D_{2h}*-symmetric diborane-like structure. Although there can be no question but that this molecule is the predominant component of the vapour, the spectrum also reveals on close scrutiny additional weak absorptions at 1923, 759, and 717 cm⁻¹, whose growth pattern indicated that they have a common origin. The carrier is clearly recognisable on the evidence of the wavenumbers and relative intensities of these IR signals as the monomeric planar GaH₃ molecule with *D_{3h}* symmetry, the spectrum being identical with those reported in earlier independent studies^{10,27} involving the co-condensation and activation of Ga atoms and H₂ with an excess of Ar.

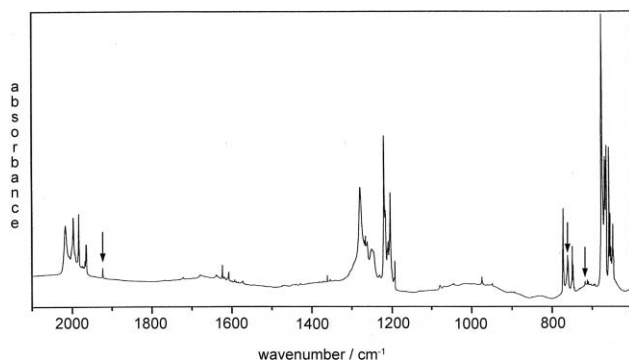
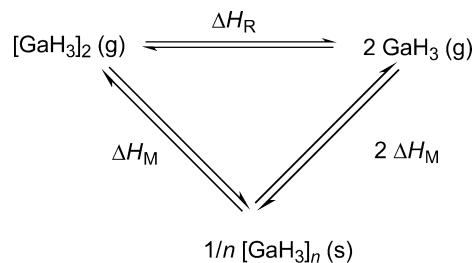


Fig. 1 The region 2100–600 cm⁻¹ in the IR spectrum of a solid Ar matrix (at *ca.* 20 K) doped with the vapour over a sample of solid gallane at 193 K. Absorptions arising from the GaH₃ monomer are distinguished by the arrows.

Similar experiments with perdeuterated gallane indicated a reduced vapour pressure for the solid relative to the isotopically natural compound at the same temperature. All but a few weak bands of the IR spectrum displayed by the resulting matrix were attributable to the Ga₂D₆ molecule.^{3,4} There was discernible, however, an additional weak band at 1388 cm⁻¹ corresponding to ν₃ (*e'*) of the GaD₃ molecule; unfortunately, the combination of low intensity and masking by more intense absorptions due to Ga₂D₆ made it impossible to detect the other two IR-active fundamentals of this molecule (expected near 545 and 518 cm⁻¹).^{10,27}

Experiments were performed with the gallane sample at different temperatures in the range 190–225 K. Each gave an IR spectrum similar to that shown in Fig. 1, but with the significant difference that the intensities of the absorptions due to GaH₃ changed relative to those of the absorptions due to Ga₂H₆, with the proportion of GaH₃ *increasing* as the temperature of the sample rose. Only when the sample temperature reached 216 K did there appear to be a discontinuity with a marked decrease in the proportion of GaH₃ present. This suggested that melting of the sample had now occurred. Neither warming nor prolonged exposure of the matrix deposit to irradiation (by the output of a 1000-W Hg–Xe arc or that of a 50-W D₂ lamp set up *in situ*) resulted in any observable changes in the IR spectrum. Accordingly, we found no evidence to suggest dissociation of Ga₂H₆/Ga₂D₆ or dimerisation of GaH₃/GaD₃ within the matrix.

The observations may be discussed in terms of the thermodynamic cycle set out in Scheme 1, where Δ*H_D* and Δ*H_M* are the enthalpies of sublimation of the dimer, Ga₂H₆, and monomer, GaH₃, respectively, and Δ*H_R* is the enthalpy change attending the dissociation of the dimer.



Scheme 1

If *p_D* and *p_M* are then used to denote the partial pressures in the vapour of the dimer and monomer, respectively, the Clausius–Clapeyron equation allows us to derive the relationship (1).

$$\frac{d \ln \left\{ \frac{p_M^2}{p_D} \right\}}{dT} = \frac{2\Delta H_M - \Delta H_D}{RT^2} = \frac{\Delta H_R}{RT^2} \quad (1)$$

Provided that the proportions of dimer and monomer trapped in the matrix reflect faithfully the composition of the vapour over the sample of solid gallane, the absorbance of an IR band such as that at 1923 or 759 cm⁻¹ due to the monomer, *A_M*, is proportional to *p_M* and that of a band, for example, at 1221 or 676 cm⁻¹ due to the dimer, *A_D*, is proportional to *p_D*. Eqn (1) may then be rewritten and integrated to give (2),

$$\ln \left\{ \frac{A_M^2}{A_D} \right\} = \frac{-\Delta H_R}{RT} + \text{constant} \quad (2)$$

and a plot of ln {*A_M*²/*A_D*} vs. 1/*T* should give a straight line with a slope affording an estimate of the enthalpy of dissociation of the gaseous Ga₂H₆ molecule, Δ*H_R*. Values of *A_M* and *A_D* were taken in practice from the *increase* in absorbance of chosen bands during deposition of the matrix for a set time. The resulting plot of ln {*A_M*²/*A_D*} vs. 1/*T* is shown in Fig. 2.

Setting aside the point corresponding to *T* = 216 K (1/*T* = 0.00463 K⁻¹), the data can be accommodated by a linear plot for

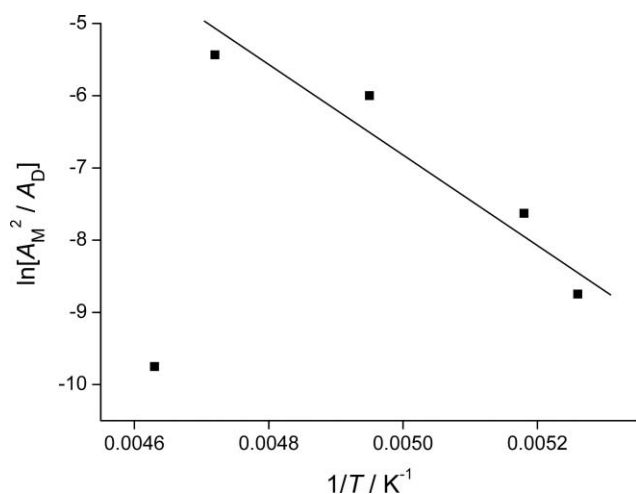


Fig. 2 Plot of $\ln \{A_M^2/A_D\}$ vs. $1/T$ for $T = 190$ – 220 K (A_M = absorbance of IR band at 1923 cm^{-1} due to GaH_3 and A_D = absorbance of IR band at 1221 cm^{-1} due to Ga_2H_6).

which the best fit gives $\Delta H_R = 59 \pm 16\text{ kJ mol}^{-1}$ ($R = 0.937$). As noted in the Experimental Section, the errant point was almost certainly associated with a phase change on the part of the gallane sample.

There are no other experimental data with which to compare directly the value of ΔH_R . ^1H NMR studies of toluene- d_8 solutions of gallane reveal at low temperatures two resonances at δ_H 4.41 and 1.11 with relative intensities in the ratio 2:1 attributable to the terminal and bridging protons of the Ga_2H_6 molecule.^{3,6} Warming to 243 K results in broadening and coalescence of the two resonances, indicating rapid exchange between terminal and bridging proton sites. The data suggest a barrier to exchange in the order of 44 kJ mol^{-1} .⁴⁰ That this rough estimate is smaller than the value we have determined for ΔH_R need come as no surprise; the mechanism of exchange in solution is unknown, but is unlikely to involve fragmentation of the dimer into two isolated GaH_3 fragments.⁴¹ Moreover, whatever pathway is involved, the effects of solvation cannot be entirely overlooked.

Previous theoretical calculations of the dissociation energy of Ga_2H_6 have given widely divergent values in the range 80 – 170 kJ mol^{-1} depending on the level of theory and the choice of basis set.^{16,18,19} The most reliable values are probably $\Delta H_e = 106.3$ and $\Delta H_0 = 91.2\text{ kJ mol}^{-1}$ deduced by Shen and Schaefer¹⁹ on the basis of CCSD methods (*cf.* B_2H_6 and Al_2H_6 for which the same calculations give $\Delta H_0 = 126$ and 129 kJ mol^{-1} , respectively). More recent, unpublished DFT calculations using the B3LYP method with a 6-311G* basis set yield for Ga_2H_6 $\Delta H_e = 92.8$ and $\Delta H_0 = \text{ca. } 78\text{ kJ mol}^{-1}$.⁴²

GED study: structure of the Ga_2H_6 molecule

The most compelling reason for undertaking a reanalysis of the original GED data for Ga_2H_6 was provided by the many advances in the treatment of the effects of vibrations on a molecular structure that have been made in the intervening years. In this reanalysis, calculated anharmonic force constants have been used to provide corrections to the experimental interatomic distances, yielding an $r_{a3,1}$ -type structure.²⁶ The $r_{a3,1}$ distances are as close

Table 1 Refined ($r_{a3,1}$) and calculated^a (r_e) geometric parameters for Ga_2H_6 from the GED study^b

	Parameter	$r_{a3,1}$	r_e	Restraint
<i>Independent</i>				
p_1	$r_{\text{Ga} \cdots \text{Ga}}$	254.86(14)	254.0	—
p_2	r_{GaH} average	163.7(6)	162.4	—
p_3	r_{GaH} difference	17.4(5)	17.8	17.8(5)
p_4	$\angle \text{H}_i\text{--Ga--H}_i$	128.6(9)	129.5	129.5(10)
<i>Dependent</i>				
p_5	$r_{\text{Ga--H}_i}$	155.0(6)	153.5	—
p_6	$r_{\text{Ga--H}_b}$	172.3(6)	171.3	—
p_7	$\angle \text{Ga--H}_b\text{--Ga}$	95.4(5)	95.7	—

^a Refers to MP2(full)/aug-cc-pVTZ calculations. ^b Distances (r) are in pm, and angles (\angle) are in degrees. See text for parameter definitions and Fig. 3 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

to equilibrium r_e distances as can be routinely achieved using corrections obtained from calculated force fields.

Four parameters were required to write a model to describe the D_{2h} -symmetric structure of Ga_2H_6 , as listed in Table 1. These were the $\text{Ga} \cdots \text{Ga}$ distance, the Ga--H_b and Ga--H_i distances (which were represented as the average of the two different distances and the difference between them), and the $\text{H}_i\text{--Ga--H}_i$ angle. Fig. 3 shows the molecular structure of Ga_2H_6 and the numbering scheme used in this study.

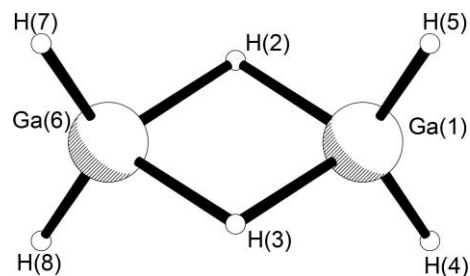


Fig. 3 Molecular structure of Ga_2H_6 including the atom-numbering scheme used in this study.

All four independent parameters, as well as three amplitudes of vibration, were refined. Calculated and experimental amplitudes of vibration for all atom pairs, along with the distance corrections applied, are listed in Table S2. SARACEN restraints²⁵ were applied to two parameters and to two amplitudes of vibration; all of these related to the hydrogen atoms which are poorly defined by the GED experiment. The final R factor for the refinement is, at $R_G = 0.155$ ($R_D = 0.096$), somewhat higher than is usual. However, taking into account the extreme conditions required for the GED experiment and the consequently high signal-to-noise ratio, this is not surprising. Visually, the goodness of fit of the radial-distribution and difference curves, as seen in Fig. 4, and the molecular-scattering intensity curves (Figure S1†) is satisfactory. The least-squares correlation matrix for the GED refinement is given in Table S3,† and coordinates for the final GED structure of Ga_2H_6 and for the calculated structure [MP2(full)/aug-cc-pVTZ] are given in Tables S4 and S5,‡ respectively.

Initial refinements of the GED data were performed using a model that allowed for the presence of varying amounts

Table 2 Comparison of selected geometric parameters for Ga₂H₆^a

Method	$r_{\text{Ga} \cdots \text{Ga}}$	r_{GaH_b}	r_{GaH_t}	$\angle \text{H}_t\text{-Ga-H}_t$	Reference
SCF/TZP	264.8	177.1	155.8	129.1	15
RHF/3-21G*	265.3	179.2	157.8	128.6	17
MP2/3-21G*	259.6	177.9	158.0	129.2	17
B3LYP/TZ2Pf	261.8	176.1	155.8	129.7	18
CCSD/DZP	260.8	175.3	155.2	129.9	19
MP2(full)/aug-cc-pVTZ	254.0	171.3	153.5	129.5	this work
GED, r_a	258.0(2)	171.0(38)	151.9(35)	130(fixed)	3
GED, $r_{a3,1}$	254.86(14)	172.3(6)	155.0(6)	128.6(9)	this work

^a Distances (r) are in pm, and angles (\angle) are in degrees.

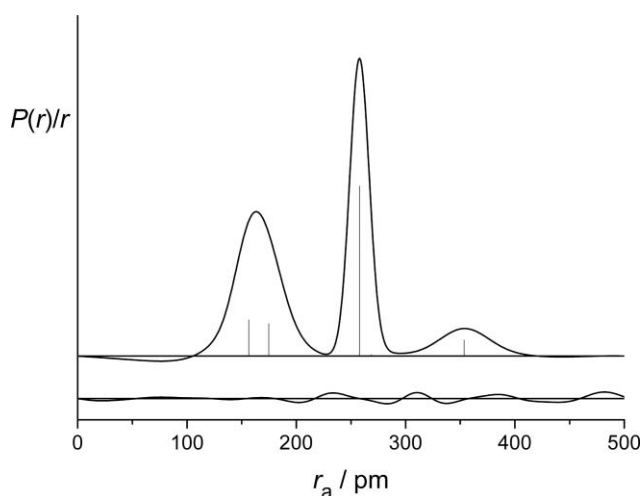


Fig. 4 Experimental radial-distribution curve and theoretical-minus-experimental difference curve for the refinement of Ga₂H₆. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.00002s^2)/(Z_{\text{Ga}} - f_{\text{Ga}})^2$.

of monomer species. However, there was no evidence of any monomer being present. That does not mean that there was none present—simply that the single parameter required to define D_{3h} -symmetric GaH₃ (a Ga–H distance) was not sufficiently well defined.

Calculations

The most striking feature of earlier quantum chemical studies^{15–19} is the complete lack of agreement between the bond lengths and interbond angles delivered by the calculations with different levels of theory and/or different basis sets. Table 2 summarises the important results from this current work and from the previous literature. For the early studies using the Hartree–Fock method,¹⁷ it is unsurprising that the distances are so poorly defined as this method ignores the effects of electron correlation. At the CCSD level,¹⁹ the bond lengths calculated are still significantly longer than those yielded by either the present calculations or analysis of the electron-diffraction data. We can only attribute the discrepancy to the adoption of an unsuitable basis set in the CCSD calculations.

It is very pleasing to note the close agreement between the geometric parameters calculated in this work [MP2(full)/aug-cc-pVTZ] and those determined from the reanalysis of the GED data. The new $r_{a3,1}$ GED structure makes use of perpendicular distance corrections obtained using an anharmonic force field. Table S2

lists these corrections ($r_a - r_c$) for each atom pair in Ga₂H₆ and it can be seen that the values range from 1.4 to 3.0 pm, indicating the large effect that vibrational motion has on this molecule.

To the best of our knowledge, every previous attempt to calculate the enthalpy change associated with the dissociation Ga₂H₆(g) → 2GaH₃(g) has ignored the basis-set superposition error (BSSE) arising from the use of finite basis sets in the calculations. In order to calculate a value with which to judge our experimental estimate, we performed calculations at the MP2(full)/aug-cc-pVTZ level. The value of ΔE_0 follows the method adopted by Shen and Schaefer¹⁹ but explicitly includes an estimate of the BSSE, which is 41 kJ mol^{−1} for this system. Therefore $\Delta E_0 = 2E_m - E_d + 2ZPE_m - ZPE_d + \text{BSSE}$, where E_m and E_d are the energies of the monomer and dimer, and ZPE_m and ZPE_d are the zero-point energy corrections for the monomer and the dimer. This gives us a value of 52 kJ mol^{−1}, which is satisfyingly close to the experimentally determined value.

Conclusions

The combination of new quantum chemical calculations at different levels of theory and current, improved methods of analysis, when applied to the results of earlier GED studies of digallane, has enabled us to determine the most realistic structure for this molecule based on the experimental data available to date. A closer approximation could be gained only by countering the lability of the compound so as to improve the quality of the data or by more extensive studies of the IR spectrum of the vapour under high resolution. Matrix-isolation experiments have identified the coexistence of a small proportion of the monomer GaH₃ with the dimer in the vapour over solid samples of gallane at temperatures in the range 190–220 K. Analysis of the relative proportions of the two molecules evaporating from the solid at different temperatures leads to a first experimental estimate of $\Delta H = 59 \pm 16$ kJ mol^{−1} for the dissociation reaction Ga₂H₆(g) → 2GaH₃(g). While significantly lower than previous theoretical valuations (80–170 kJ mol^{−1}),^{16,18,19} this result is in good accord with an estimate of 52 kJ mol^{−1} gained from fresh calculations at the MP2(full)/aug-cc-pVTZ level.

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References

- 1 E. Wiberg and T. Johannsen, *Naturwissenschaften*, 1941, **29**, 320; E. Wiberg and T. Johannsen, *Angew. Chem.*, 1942, **55**, 38–40; E. Wiberg, T. Johannsen and O. Stecher, *Z. Anorg. Allg. Chem.*, 1943, **251**, 114–124; E. Wiberg and M. Schmidt, *Z. Naturforsch.*, 1952, **7B**, 577.
- 2 A. J. Downs, M. J. Goode and C. R. Pulham, *J. Am. Chem. Soc.*, 1989, **111**, 1936–1937.
- 3 C. R. Pulham, A. J. Downs, M. J. Goode, D. W. H. Rankin and H. E. Robertson, *J. Am. Chem. Soc.*, 1991, **113**, 5149–5162.
- 4 P. F. Souter, L. Andrews, A. J. Downs, T. M. Greene, B. Ma and H. F. Schaefer, III, *J. Phys. Chem.*, 1994, **98**, 12824–12827.
- 5 J. M. Dyke, D. Haggerston, O. Warschkow, L. Andrews, A. J. Downs and P. F. Souter, *J. Phys. Chem.*, 1996, **100**, 2998–3004.
- 6 A. J. Downs and C. R. Pulham, *Adv. Inorg. Chem.*, 1994, **41**, 171–232.
- 7 A. J. Downs and C. R. Pulham, *Chem. Soc. Rev.*, 1994, **23**, 175–184.
- 8 A. J. Downs, *Coord. Chem. Rev.*, 1999, **189**, 59–100.
- 9 S. Aldridge and A. J. Downs, *Chem. Rev.*, 2001, **101**, 3305–3365.
- 10 X. Wang and L. Andrews, *J. Phys. Chem. A*, 2003, **107**, 11371–11379.
- 11 L. Andrews and X. Wang, *Science*, 2003, **299**, 2049–2052; X. Wang, L. Andrews, S. Tam, M. E. DeRose and M. E. Fajardo, *J. Am. Chem. Soc.*, 2003, **125**, 9218–9228; L. Andrews and X. Wang, *J. Phys. Chem. A*, 2004, **108**, 4202–4210.
- 12 L. Andrews and X. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 1706–1709; X. Wang and L. Andrews, *J. Phys. Chem. A*, 2004, **108**, 4440–4448.
- 13 X. Wang and L. Andrews, *J. Phys. Chem. A*, 2004, **108**, 3396–3402.
- 14 P. Hunt and P. Schwerdtfeger, *Inorg. Chem.*, 1996, **35**, 2085–2088.
- 15 C. Liang, R. D. Davy and H. F. Schaefer, III, *Chem. Phys. Lett.*, 1989, **159**, 393–398.
- 16 K. Lammertsma and J. Leszczyński, *J. Phys. Chem.*, 1990, **94**, 2806–2809.
- 17 B. J. Duke, *THEOCHEM*, 1990, **208**, 197–204.
- 18 C. W. Bock, M. Trachtman, C. Murphy, B. Muschert and G. J. Mains, *J. Phys. Chem.*, 1991, **95**, 2339–2344; V. Barone, C. Adamo, S. Fliszár and N. Russo, *Chem. Phys. Lett.*, 1994, **222**, 597–602; V. Barone, L. Orlandini and C. Adamo, *J. Phys. Chem.*, 1994, **98**, 13185–13188.
- 19 M. Shen and H. F. Schaefer, III, *J. Chem. Phys.*, 1992, **96**, 2868–2876.
- 20 C. R. Pulham, A. J. Downs, E. Johnsen, S. Parsons and P. F. Souter, unpublished work.
- 21 J. W. Turley and H. W. Rinn, *Inorg. Chem.*, 1969, **8**, 18–22.
- 22 A. J. Downs, T. M. Greene, E. Johnsen, P. T. Brain, C. A. Morrison, S. Parsons, C. R. Pulham, D. W. H. Rankin, K. Aarset, I. M. Mills, E. M. Page and D. A. Rice, *Inorg. Chem.*, 2001, **40**, 3484–3497.
- 23 O. Bastiansen and M. Trætteberg, *Acta Crystallogr.*, 1960, **13**, 1108–1108; H. Breed, O. Bastiansen and A. Almenningen, *Acta Crystallogr.*, 1960, **13**, 1108–1108; Y. Morino, *Acta Crystallogr.*, 1960, **13**, 1107–1107.
- 24 V. A. Sipachev, *THEOCHEM*, 1985, **121**, 143–151; V. A. Sipachev, in *Advances in Molecular Structure Research*, ed. I. Hargittai and M. Hargittai, JAI Press, Greenwich, 1999, vol. 5, pp. 323–371.
- 25 A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson and B. A. Smart, *J. Phys. Chem.*, 1996, **100**, 12280–12287; P. T. Brain, C. A. Morrison, S. Parsons and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1996, 4589–4596; N. W. Mitzel and D. W. H. Rankin, *Dalton Trans.*, 2003, 3650–3662.
- 26 P. D. McCaffrey, R. J. Mawhorter, A. R. Turner, P. T. Brain and D. W. H. Rankin, *J. Phys. Chem. A*, 2007, **111**, 6103–6114.
- 27 P. Pullumbi, Y. Bouteiller, L. Manceron and C. Mijoule, *Chem. Phys.*, 1994, **185**, 25–37.
- 28 See, for example, H.-J. Himmel, A. J. Downs, T. M. Greene and L. Andrews, *Organometallics*, 2000, **19**, 1060–1070.
- 29 National Service for Computational Chemistry Software (NSCCS). URL <http://www.nscs.ac.uk>.
- 30 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.
- 31 C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618–622.
- 32 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261; P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222; M. S. Gordon, *Chem. Phys. Lett.*, 1980, **76**, 163–168.
- 33 T. H. Dunning, Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- 34 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.
- 35 V. Barone, *J. Chem. Phys.*, 2004, **120**, 3059–3065; V. Barone, *J. Chem. Phys.*, 2005, **122**, 014108/1–014108/10.
- 36 C. M. Huntley, G. S. Laurensen and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1980, 954–957.
- 37 H. Fleischer, D. A. Wann, S. L. Hinchley, K. B. Borisenko, J. R. Lewis, R. J. Mawhorter, H. E. Robertson and D. W. H. Rankin, *Dalton Trans.*, 2005, 3221–3228.
- 38 S. L. Hinchley, H. E. Robertson, K. B. Borisenko, A. R. Turner, B. F. Johnston, D. W. H. Rankin, M. Ahmadian, J. N. Jones and A. H. Cowley, *Dalton Trans.*, 2004, 2469–2476.
- 39 A. W. Ross, M. Fink and R. Hilderbrandt, in *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, The Netherlands, vol. C, 1992, pp. 245–338.
- 40 C. R. Pulham, D.Phil. thesis, University of Oxford, 1991, and unpublished results.
- 41 J. R. Kolb and T. J. Marks, *Chem. Rev.*, 1977, **77**, 263–293.
- 42 H.-J. Himmel, unpublished results.